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(71) Applicant: **MONSANTO COMPANY**

**St. Louis, Missouri 63167 (US)**

(72) Inventor:

**The designation of the inventor has not yet been  
filed**

(74) Representative:

**Bosch, Henry et al  
Monsanto Services International S.A.  
Patent Department  
Avenue de Tervuren 270/272  
Letter Box No. 1  
1150 Brussels (BE)**

(54) **Method for the manufacture of photovoltaic cell**

(57) The technology of this invention relates to a commercially attractive manufacturing method for photoelectrochemical cells. In essence, a photovoltaic ink suspension, containing essentially polycrystalline semiconductor dye coated particles, a hydrolyzable semiconductor precursor alkoxide and an inert solvent, is applied to a conductor area followed by in situ treatment of the ink to yield a semi-conductor effective layer for use in a photovoltaic cell.

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## Description

The technology of this patent application relates to a method for the manufacture of a photovoltaic cell which can be used for converting incident light into electrical energy. The method basically comprises applying a photovoltaic ink consisting essentially of a suspension of the dye-coated particles of the semi-conductor functional layer, a hydrolyzable semi-conductor precursor, such as a hydrolyzable metal alkoxide, and an inert, in relation to the metal alkoxide, solvent, is applied to a substrate provided with conductor patterns, to thereby generate under temperature conditions not exceeding 180 °C, a semiconductor functional layer for use in a regenerative photovoltaic cell.

The prior art relating to regenerative photovoltaic cells is crowded and diverse and is possessed, in addition to detailed proposals concerning mechanisms underlying the conversion of light to electrical energy, of methods for the manufacture of such cells, particularly the semi-conductor functional part, which relays and regulates the transport of photoexcited electrons from the chromophore dye to the anode conductor. EP-A-0 333 641 describes photo-electrochemical cells having a polycrystalline metal oxide semi-conductor with a monomolecular chromophore layer in its surface region. At least one of the electrodes shall be transparent to the incident light. The cells are of the dual substrate "sandwich-type" configuration having oppositely charged current collectors attached to distinct substrates. The semi-conductor part is provided with sintered (electrically conductive) nano-cells, such as  $\text{TiO}_2$ . The cells are made by depositing sequentially minimal amounts of semi-conductor precursors followed by high temperature sintering after each deposition of precursor Kavan et al., J. of The Electrochemical Society, February 1996, pages 394-400, have reported that sintering can reduce the (BET) surface area of nanocrystalline  $\text{TiO}_2$  and henceforth its photoelectrochemical conversion functionality. Péchy et al., J. Chem. Soc., Chem. Commun., 1995, pages 65-66, describe the preparation of phosphonated polypyridyl ligands which are reported to exhibit excellent charge-transfer sensitizer properties for nanocrystalline  $\text{TiO}_2$  film application. These characteristics render the phosphonated polypyridyl ligands particularly attractive for application in molecular photovoltaic devices.

Hanprasopwattana et al., Langmuir 1996, 12, 3173-3179, describe methods of uniformly distributing monolayer to multilayer films of titania on mono-disperse silica spheres. The titania coatings so deposited are amorphous. Heating to temperatures around 500°C is needed to convert the amorphous coating into polycrystalline  $\text{TiO}_2$ . Kay et al., The Journal of Physical Chemistry 1996, Vol. 98, pages 952-959, report on the mechanism of photosensitization of transparent  $\text{TiO}_2$  electrodes with chlorophyll derivatives, particularly induced photocurrent phenomena. Grätzel et al., Cur-

rent Science, Vol. 66, No. 10, 25 May 1994, describe properties and requirements of efficient dye-sensitized photoelectrochemical cells for direct conversion of visible light to current. The authors conclude that actual cell technology (at the date of the paper) is not sufficient and cannot lead to commercially viable executions. McEvoy et al., Solar Energy Materials and Solar Cells 32 (1994) 221-227, summarize general principles and the historical development sequence concerning photovoltaic technologies.

While substantial efforts were invested towards providing economically acceptable manufacturing technology for photoelectrochemical cells, these developments efforts have not yielded, as of yet, acceptable solutions, in particular meaningful improvements to current photovoltaic cell making technology.

It is therefore a main object of this invention to make available a simplified and reliable method for the manufacture of photovoltaic cells. It is a further object of this invention to generate a method for the manufacture of photovoltaic cells whereby the semi-conductor functional layer can be produced/deposited in a relatively simple arrangement without a need for using extreme, possibly repetitive, conditions such as sintering temperatures. It is still another object of this invention to provide a high speed, as compared to previous methods, manufacturing process for photovoltaic cells. Yet another object of this invention aims at economically producing semi-conductor functional layers for use in photovoltaic cells. It is still another object of this invention to provide a method for the manufacture of photovoltaic cells which does not require extreme conditions of temperature and/or elaborate control of the surrounding atmosphere. The foregoing and other objects of this invention can now be met beneficially with the aid of the manufacturing arrangement of this invention.

This invention, in part, relates to a method for the manufacture of regenerative photovoltaic cells containing substrates, current collectors and dye-coated semi-conductor functional layer, wherein a photovoltaic ink consisting essentially of a suspension of agglomerates of the dye-coated semi-conductor functional particles, a hydrolyzable semiconductor precursor, and an inert solvent, is applied to a conductor functional substrate e.g. a substrate provided with conductor patterns to thereby generate under temperature conditions not exceeding 180 °C, a semi-conductor functional layer.

The semi-conductor particle in the dye-coated particles capable of exhibiting semi-conductor functionality can preferably be represented by polycrystalline metal oxides of titanium, zirconium, hafnium, strontium, zinc, indium, tin, antimony, yttrium, lanthanum, vanadium, niobium, tantalum, chromium, molybdenum, tungsten, iron, nickel, silver and mixtures of such metal oxides. The metal in the metal alkoxides can be selected from the preferred metals which can be used in the polycrystalline (semi) conductor metal oxides. The ink can, in addition to the essential metal alkoxide, contain, as an

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conductor functionality. Preferred metals, for use in the hydrolyzable alkoxides herein, belong to groups IIb, IVb, Vb, VIb, IIIa, IVa and Va of the Mendeleev table of elements. The preparation of the alkoxides is well known in the technical community. In fact, the majority, if not all, of the metal alkoxides for use herein are known and commercially available materials. The alkoxide moiety can be represented by species having, for example, from 1-10 carbon atoms. Specific examples of the like alkoxides include methoxide, ethoxide, propoxide, isopropoxide, butoxide a.s.o. The hydrolyzable metal alkoxides, which correspond to the hydrolyzable semi-conductor precursor, are generally employed in levels ranging from 0.1% to 15%, preferably 0.2% to 10%, expressed on the same basis as the dye-coated metal oxide particles. In a preferred embodiment, it can be beneficial to incorporate, in addition to the hydrolyzable semi-conductor precursor, a low level such as from  $10^{-6}\%$  to 10%, expressed in relation to the hydrolyzable semi-precursor metal alkoxide (100%), of a further (non semi-conductor) metal alkoxide selected from silicium, aluminum, germanium, and boron.

The inert solvent is generally used in levels ranging from 6% to 85%, preferably from 10% to 80%, expressed on the same level as the metal oxide particles. The term inert means that the solvent is not capable of reacting with the metal or metalloid alkoxides present in the ink suspension under ambient (20 °C) storage conditions for a period of 6 months. Examples of suitable solvents include straight and branched alkanes having from 8 to 20 carbon atoms, aromatic alkylates having from 4 to 12 carbon atoms in the straight or branched alkyl chain, ethers or ketones having from 8 to 24 carbon atoms and blends thereof.

The ink suspension can further contain additive levels i.e. 0.1% to 2.0%, of various optional performance and compatibilizing agents which are used for their known functionality. Such additives can serve to enhance the functionality of any one of the essential ternary ingredients in the ink suspension. Examples of the like additives can be represented by dispersants which can enhance the even distribution of the ink particles on the substrate.

The suspension shall be distributed onto the substrate provided with conductive patterns by methods generally known inclusive of printing, roll deposition or deposition with a doctor blade to thereby yield a uniform layer of ink. The so deposited layer of the precursor ink will be treated under mild and non-destructive conditions including temperatures below 180 °C, preferably below 150 °C, possibly combined with non destructive pressures e.g. below 20 bars, and/or evaporation under sub-atmospheric pressures. So proceeding will yield an effective semi-conductor functional grid which can control and promote the transport of electrons originating from the chromophore dye to the conductive layer. The actual and combined optimization of physical conditions required for converting the ink suspension into an effective

semi-conductor grid are routine measures. In a preferred execution, the support of the deposited layer has a conductivity of than 10 ohm per square to achieve an appropriate and beneficial level of photochemical performance.

In a preferred embodiment, the core of the aggregates of the dye-coated particles can be represented by inactive metal oxides particles such as alumina and silica provided, of course, that such inactive core is coated with a semi-conductor functional layer comprising a metal oxide semi-conductor wherein the metal is selected from titanium, zirconium, hafnium, strontium, zinc, indium, yttrium, lanthanum, vanadium, niobium, tantalum, chrome cadmium, antimony, tin, molybdenum, tungsten and mixtures of two or more of these metal oxides. The term "inactive" as used in that context means that the particular metal oxide e.g. silica and/or alumina does not exhibit semi-conductor properties upon use in a photovoltaic cell manufactured in accordance with the method of this invention. The from a semi-conductor standpoint inactive core can represent up to 80%, preferably up to 60% of the aggregates of dye-coated particles.

The substrate for use in the cell manufactured in accordance with this invention can be represented by conventional substrate materials. Such materials can be selected from flexible or rigid, mineral or organic materials, such as synthetic and natural polymers and combinations thereof, paper, wood, glass, aluminum, tin, nickel, iron, zinc, copper, cloth, fibers and mixtures thereof.

In another execution of the cell made by the method herein, a minor proportion of semi-conductor particles is embedded into the anode conductor. Preferably from 1% to 10% by weight, expressed versus the conductive material (100%), of the said semi-conductor particles are embedded into the conductive material layer. In another execution herein, the anode conductor is provided with a supplementary layer of semi-conductor metal oxides before applying the photovoltaic ink. This supplementary layer is deposited by known means and is electronically interconnected with the anode conductor.

The photovoltaic cells manufactured in accordance with the method of this invention can be used beneficially for converting incident light into electrical energy. Visible light generally having a wave-length in the range of from 300 nms to 900 nms (nms = nanometer), preferably daylight having a wave-length in the range of from 400 nms to 700 nms are for obvious reasons prime sources of light. It is understood, however, that the cell in accordance with this invention can be manufactured and correspondingly optimized with whatever source of light energy is available.

## Claims

1. A method for the manufacture of photovoltaic cell

containing a substrate, current collectors, dye coated semi-conductor functional layer wherein a photovoltaic ink consisting essentially of a suspension of the dye coated particles of the semi-conductor functional layer, a hydrolyzable semi-conductor precursor, such as a hydrolyzable metal alkoxide, and an inert, in relation to the metal alkoxide, solvent, is applied to a substrate provided with conductor patterns to thereby generate, under temperature conditions not exceeding 180 °C, a semi-conductor functional layer.

anode conductor is provided with a supplementary layer of semi-conductor oxides before applying the photovoltaic ink.

2. The method in accordance with Claim 1 wherein the ink is deposited onto the substrate.

3. The method in accordance with Claim 1 wherein the metal in the metal alkoxide is selected from titanium, zirconium, hafnium, strontium, zinc, indium, yttrium, lanthanum, vanadium, niobium, tantalum, chrome, cadmium, antimony, tin molybdenum and tungsten or mixtures of these metal alkoxides.

4. The method in accordance with Claim 3 wherein, in addition, a further metal alkoxide is present selected from silicon, aluminum, germanium and boron in a level of from  $10^{-6}\%$  to 10%, expressed in relation to the metal alkoxide (100%).

5. The method in accordance with Claim 1 wherein the particle is represented by inert, photochemically and electrically inactive within the context of this method, material, such as silica or alumina, coated with a semi-conductor functional layer comprising a metal oxide semi-conductor wherein the metal is selected from titanium, zirconium, hafnium, strontium, zinc, indium, yttrium, lanthanum, vanadium, niobium, tantalum, chrome, cadmium, antimony, tin molybdenum and tungsten or mixtures of these metals.

6. The method in accordance with Claim 1 wherein the substrate is selected from flexible or rigid, mineral or organic materials, such as synthetic and natural polymers and combinations thereof, paper, wood, glass, aluminum, tin, nickel, copper, cloth, fibers and mixtures thereof.

7. The method according to Claim 1 wherein the photovoltaic ink is deposited onto the substrate containing anode and cathode conductors to provide ohmic contact between the photovoltaic layer and the anode conductor to thus yield a single substrate cell or on an individual substrate provided with anode conductor to thus yield, in combination with another substrate provided with the cathode conductor, a sandwich-type cell.

8. The method according to Claim 7 wherein the

9. The method according to Claim 7 wherein the anode conductor contains from 1% to 10% by weight, expressed versus the conductive material (100%), of semi-conductor metal oxide particles.



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## EUROPEAN SEARCH REPORT

Application Number  
EP 97 87 0021

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A	DE 42 25 575 A (ABB PATENT GMBH) 10 February 1994 * column 1, line 60 - column 2, line 45 * ---	1-3,6,7	H01G9/20
A	DE 44 21 978 A (PENTH BERND DR) 4 January 1996 * column 3, line 65 - column 4, line 33 * -----	1-3,6,7	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			H01G
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 16 July 1997	Examiner Schuermans, N
<p><b>CATEGORY OF CITED DOCUMENTS</b></p> <p>X : particularly relevant if taken alone  Y : particularly relevant if combined with another document of the same category  A : technological background  O : non-written disclosure  P : intermediate document</p> <p>T : theory or principle underlying the invention  E : earlier patent document, but published on, or after the filing date  D : document cited in the application  L : document cited for other reasons</p> <p>-----  &amp; : member of the same patent family, corresponding document</p>			

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